mated 15 cal. mole^{-1} deg.$^{-1}$ of internal heat capacity in ReO_4^- if the solvent interactions between Cl^-(aq) and ReO_4^-(aq) are to be compared. The remaining net difference of 13 cal. mole^{-1} deg.$^{-1}$ does not seem so large that it cannot be accounted for reasonably by one or two water molecules less of primary hydration in ReO_4^- (aq) than are present in Cl^-(aq).

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The Thermodynamic Properties of High Temperature Aqueous Solutions. III. The Partial Molal Heat Capacities of Hydrochloric Acid from 0 to 100° and the Third-Law Potentials of the Silver–Silver Chloride and Calomel Electrodes from 0 to 100°[1]

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The heat capacities of aqueous hydrochloric acid from 0 to 100° have been calculated from previous data in the literature. These heat capacity data are used in combination with the cell potentials of the silver–silver chloride electrode from 0 to 100° to derive third-law potentials and new thermodynamic functions of the chloride ion. A similar treatment is applied to the less complete data of the calomel electrode system.

Introduction

In the previous paper of this series,[3] the thermodynamic properties of aqueous sodium perrhenate and perrhenic acid at infinite dilution were determined from 0 to 100° by the integral heat method.[4] In effect, these measurements established the thermodynamic differences between H^+(aq) and Na^+(aq) over this range of temperature. When combined with previous data on NaCl(aq),[4] values of $\overline{C}_{p_2}°$ for the important electrolyte HCl(aq) can be derived.

This communication also describes an interesting application of electrolyte heat capacity data to the examination of electrode systems at elevated temperatures. As far as can be determined, this is the first instance where third-law potentials have been derived from cell measurements and heat capacities involving aqueous systems. Such a procedure provides a powerful method of investigating the reliability of chemical cells.

The Heat Capacity of HCl(aq)

The heat capacity data required to generate values of $\overline{C}_{p_2}°$ for HCl(aq) have been published[3,4]: $\overline{C}_p°_{(HCl)} = \overline{C}_p°_{(HReO_4)} - \overline{C}_p°_{(NaReO_4)} + \overline{C}_p°_{(NaCl)}$. Values of the heat capacities of HCl(aq) are given in Table I,

TABLE I
PARTIAL MOLAL HEAT CAPACITIES FOR HYDROCHLORIC ACID

t, °C.	$-\overline{C}_{p_2}°$, cal. mole^{-1} deg.$^{-1}$	t, °C.	$-\overline{C}_{p_2}°$, cal. mole^{-1} deg.$^{-1}$
0[a]	56.2	50	30.2
5	40.7	60	31.6
10	34.7	70	33.9
20	31.2	80	36.9
25	30.5	90	40.3
30	30.2	100[a]	45.8
40	30.0		

[a] From extrapolated values.

calculated from smoothed functions for the other three electrolytes involved. The errors in the tabulated

values of $\overline{C}_{p_2}°$ should be less than 1 cal. mole^{-1} deg.$^{-1}$ at all temperatures except at 0 and 100°.

Previous values of $\overline{C}_{p_2}°$ of HCl(aq) have been reported.[5-9] The best data at 25° appear to be those of Gucker and Schminke,[5] who report $\overline{C}_{p_2}° = -29.2$ cal. mole^{-1} deg.$^{-1}$ at 25°. Three other compilations list -29.2[10] and -30 cal. mole^{-1} deg.$^{-1}$,[8,11] the latter apparently from a revised extrapolation of previous specific heat and other thermodynamic data.

The situation with regard to the present "integral heat" data and previously[9] published $\overline{C}_{p_2}°$ data on HCl(aq) at temperatures other than 25° is illustrated in Fig. 1. The quantitative agreement is not very good. Part of the difference can be attributed to the well-known difficulty in extrapolating specific heat data from higher concentrations. Further, the authors of these data chose the older[6,7] and more negative values of $\overline{C}_{p_2}°$ at 18 and 25° as a guide in these extrapolations to infinite dilution. In addition, however, it seems apparent that some small but important systematic error has entered into the previous specific heat measurements. A very small error in specific heats leads to much larger errors in ϕ_{c_p} and $\overline{C}_{p_2}°$.

It is of interest to note the experimental problem in obtaining partial molal heat capacity data. Specific heat measurements are easier to make in the sense that a larger amount of data can be obtained in a shorter time than required to make the detailed concentration calorimetric study of the heats of solution. However, a precision some ten times greater is required in specific heat measurements, if the dilute (≤ 0.1 m) region of electrolyte behavior is to be studied. Unfortunately, extrapolation of ϕ_{c_p} from this region is still largely empirical. The present HCl(aq) system leads us to

(1) Supported by a grant from the Atomic Energy Commission.

(2) From the Ph.D. Thesis of J. C. Ahluwalia, Purdue University, June, 1963.

(3) J. C. Ahluwalia and J. W. Cobble, *J. Am. Chem. Soc.*, **86**, 5377 (1964).

(4) C. M. Criss and J. W. Cobble, *ibid.*, **83**, 3223 (1961).

(5) F. T. Gucker and K. H. Schminke, *ibid.*, **54**, 1358 (1932).

(6) M. Randall and W. D. Ramage, *ibid.*, **51**, 729 (1929).

(7) F. D. Rossini, *J. Res. Natl. Bur. Std.*, **1**, 47 (1931); **6**, 679 (1932).

(8) National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

(9) E. Wicke, M. Eigen, and Th. Ackermann, *Z. Physik. Chem.* (Frankfurt), **1**, 340 (1954).

(10) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 354.

(11) G. N. Lewis and M. Randall, "Thermodynamics," 2nd Ed., revised by K. S. Pitzer and Leo Brewer, McGraw-Hill Book Co., New York, N. Y., 1961, pp. 400, 652.
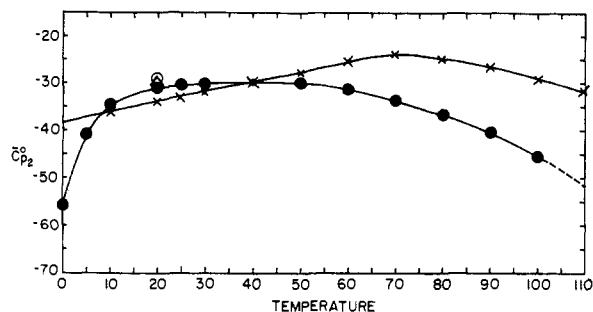
Fig. 1.—The partial molal heat capacity of HCl(aq): the solid circles are from this research based on the integral heat method; the crosses are from ref. 9 and are based on specific heat data of concentrated solutions; the open symbols are reported values based on specific heat (ref. 5) and specific heat and other thermodynamic data (ref. 8).

believe that specific heat measurements provide interesting qualitative information on the temperature behavior of $\overline{C_{p_2}}^\circ$, but very little quantitative data. It should be noted, however, that the agreement between the two kinds of $\overline{C_{p_2}}^\circ$ data was much better in the case of NaCl(aq).[4,12]

Third-Law Potentials of the Silver–Silver Chloride Electrode

The availability of accurate values of $\overline{C_{p_2}}^\circ$ on HCl(aq) provides a valuable opportunity to critically examine the very important silver–silver chloride electrode system. This electrode has been the subject of a great deal of study and represents one of the best examples of a thermodynamically reversible system.[13] The most extensive data below 100° are the very carefully done series of measurements of Bates and Bower[14] between 0 and 95°, and the data of Harned and Ehlers[15] from 0 to 60°.

The standard potential of a cell, E°_T, at some temperature, T, is related to the corresponding potential at 25°, E°_{25}, by eq. 1.

$$E^\circ_T = E^\circ_{25} + \frac{1}{nF}\left[\Delta S^\circ_{25}\Delta T - \int_{298}^{T} \Delta C_p{}^\circ dT + T\int_{298}^{T} \Delta C_p{}^\circ \frac{dT}{T}\right] \quad (1)$$

If $\Delta C_p{}^\circ$ is known, or even reliably estimated, for the cell reaction between 25° and T, then E°_{25} and ΔS°_{25} can be treated as adjustable parameters which best fit all of the experimental values of E°_T. Such a procedure can be called the "third-law" method of deriving E°_{25} and ΔS°_{25} since it ultimately depends upon the fact that heat capacities must go to zero at 0°K.

The cell reaction involved is

$$\text{aq.} + \text{AgCl(c)} + 0.5\text{H}_2(\text{g}) = \text{Ag(c)} + \text{HCl(aq)} \quad (2)$$
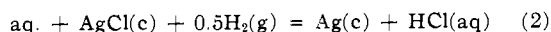
The heat capacities of AgCl(c), $\text{H}_2(\text{g})$, and Ag(c) have been tabulated elsewhere.[16] Data on the heat capacity of HCl(aq) are from Table I.

(12) M. Eigen and E. Wicke, Z. Elektrochem., 55, 354 (1951).

(13) For a summary of electrochemical data on this system, see ref. 10, Chapter 11, and ref. 14.

(14) R. G. Bates and V. E. Bower, J. Res. Natl. Bur. Std., 53, 283 (1954).

(15) Reference 13, p. 456.

(16) K. K. Kelley, U. S. Bureau of Mines Bulletin 584, U. S. Government Printing Office, Washington, D. C., 1960.
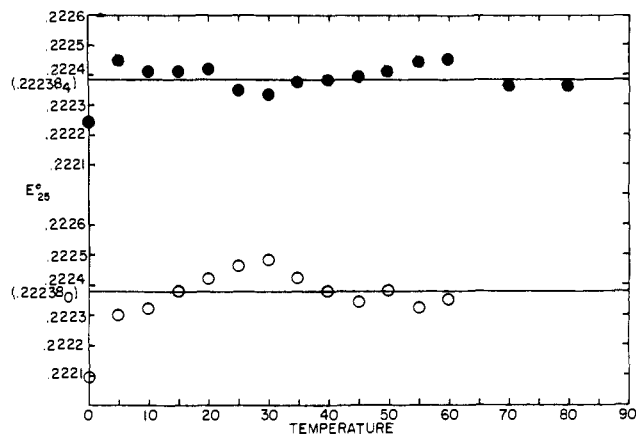
Fig. 2.—Third-law analysis of the potentials of the silver–silver chloride electrode: the lower values of E°_{25} are from the data of Harned and Ehlers,[15] and the upper values are from Bates and Bower[14]; the straight lines represent the least-squares values of E°_{25} derived from each set of data and eq. 3.

Equation 1 can be rearranged as

$$E^\circ_T + \frac{1}{nF}\left[\int_{298}^{T}\Delta C_p{}^\circ dT - T\int_{298}^{T}\Delta C_p{}^\circ \frac{dT}{T}\right] = E^\circ_{25} + \frac{\Delta S^\circ_{25}}{nF}\Delta T \quad (3)$$

Thus E°_{25} and ΔS°_{25} can be evaluated graphically by plotting the left side of eq. 3 against ΔT. The slope of such a plot gives $\Delta S^\circ/nF$ and the value of E°_{25} can be obtained at $\Delta T = 0$. Actually, for data of the accuracy being discussed, it is not convenient to evaluate E° and ΔS°_{25} graphically. Consequently, a linear least-squares treatment of both sets of cell data[14,15] was made using eq. 3. The result of such a calculation gives $E^\circ_{25} = 0.222384$ v. and $\Delta S^\circ_{25} = -14.86$ cal. mole^{-1} deg.$^{-1}$ for the Bates and Bower[14] data, and $E^\circ_{25} = 0.222380$ v. and $\Delta S^\circ_{25} = -14.88$ cal. mole^{-1} deg.$^{-1}$ from the data of Harned and Ehlers.[15] The standard potentials at 25° thus generated by this analysis from the two sets of data agree to within 0.004 mv., a truly remarkable situation. The analysis is best illustrated by reference to Fig. 2, where values of E°_{25} generated from each E°_T measurement at a different temperature are indicated for the two sets of data.

Figure 2 illustrates that the two sets of data are essentially in agreement; to merely compare potentials at one temperature, as has been done in the past, can be misleading. While the data of Harned and Owen show a nonrandom pattern of deviation which is the cause of the larger errors in E°_{25} and ΔS°_{25} obtained from their measurements, the close agreement of the thermodynamic data from the two sources leaves little to be desired. We recommend adoption of $E^\circ_{25} = 0.22384$ v. and $\Delta S^\circ_{25} = -14.86$ cal. mole^{-1} deg.$^{-1}$ for the silver–silver chloride electrode. The sixth significant figure in the potential is somewhat uncertain not only because of the errors in obtaining E°_T, but also because the temperature of the electrodes involved was usually known (on the average) to no better than $\pm 0.02°$.

It should be pointed out that the commonly accepted entropies for all of the substances[8] involved in eq. 2 lead to a ΔS°_{25} for the silver–silver chloride electrode of

TABLE II

THIRD-LAW POTENTIALS OF THE SILVER-SILVER CHLORIDE ELECTRODE

t, °C.	$E°_{T(obsd)}$,[a] v.	$E°_{T(obsd)}$, v.[b]	$\int_{298}^{T} \Delta C°_p\, dT$, cal. T	$\int_{298}^{T} \Delta C_p°\, dT/T$, cal.	$E°_{25}$, v.[c] (from col. 2)	$E°_{25}$, v.[c] (from col. 3)	$E°_T$, v.[d] (calcd.)
0	0.23655	0.23642	1137.2	1095.6	0.22224	0.22209	0.23668
5	0.23413	0.23400	851.8	824.0	0.22245	0.22230	0.23406
10	0.23142	0.23134	619.2	604.1	0.22241	0.22232	0.23139
15	0.22857	0.22855	406.2	399.7	0.22241	0.22238	0.22854
20	0.22557	0.22558	201.1	199.5	0.22242	0.222425	0.22553
25	0.22234	0.22246	0.0	0.0	0.22234	0.22246	0.22238
30	0.21904	0.21919	−199.25	−200.8	0.22233	0.222485	0.21909
35	0.21565	0.21570	−397.85	−404.3	0.22237	0.222425	0.21566
40	0.21208	0.21207	−596.45	−611.1	0.22238	0.22238	0.21200
45	0.20835	0.20828	−795.2	−821.8	0.22239	0.22234	0.20834
50	0.20449	0.20444	−994.95	−1036.7	0.22241	0.22238	0.20446
55	0.20056	0.20042	−1197.3	−1256.0	0.22244	0.222325	0.20050
60	0.19649	0.19636	−1403.8	−1482.5	0.22245	0.22235	0.196415
70	0.18782		−1833.9	−1961.7	0.22236		0.18784
80	0.17873		−2290.9	−2480.0	0.22236		0.17874
90	0.16952		−2781.45	−3045.55	0.22285		0.16905
95	0.16511		−3040.7	−3349.2	0.22359		0.16390
100			−3314.2	−3669.8			0.15863

[a] Data from ref. 14. [b] Data from ref. 15. [c] Based on the value of $\Delta S°_{25} = -14.86$ cal. mole^{-1} deg.$^{-1}$. [d] Based on the values of $E°_{25} = 0.22238$ v. and $\Delta S°_{25} = -14.86$ cal. mole^{-1} deg.$^{-1}$.

−15.21 cal. mole^{-1} deg.$^{-1}$, now clearly demonstrated as unacceptable. Since there is little reason to doubt that the entropies of the pure substances (silver, silver chloride, and hydrogen) are in error, present treatment essentially changes the entropy of HCl(aq), i.e., chloride ion. The new value for this latter species becomes +13.51 cal. mole^{-1} deg.$^{-1}$.[17] The number of thermochemical values based on the present value of 13.16 cal. mole^{-1} deg.$^{-1}$ which should now be changed must be sizeable.

The entropy of HCl(aq) is not the only function so involved. While activity coefficients at each temperature will probably not be changed appreciably by use of the new recommended values of $E°_T$ in Table II, those functions which depend upon differences in $E°_T$ values at several temperatures can be affected. New values of $\overline{L}_2$ will probably be different, and $\overline{J}_2°$ will almost certainly change significantly.

Above 80°, the present analysis clearly indicates that some additional factor is adversely affecting the measured potentials. Conceivably, this could be due to the increasing solubility of silver chloride, although other effects could also be involved. This same trend toward potentials too positive can also be noticed in the more recent higher temperature data of Greeley, et al.[18] Preliminary estimates indicate that these errors might run as large as a few millivolts. The last column of Table II lists the calculated values for the potential up to 100°, based on the present analysis, and extrapolated values of $C_{p_2}°$ for HCl(aq) above 90°. These potentials should provide an excellent basis for a standard reference electrode in aqueous solution up to 80°; at higher temperatures the experimental electrode is not, at present, very satisfactory.

The Calomel Electrode

A similar analysis can be carried out on another electrode of interest in solutions above 25°. The calomel electrode is apparently capable of very reproducible potentials, although its usable temperature range is limited because of disproportionation of Hg_2Cl_2 at higher temperatures. The cell reaction involved is

$$\text{aq.} + 0.5Hg_2Cl_2(c) + 0.5H_2(g) = Hg(l) + HCl(aq) \quad (4)$$
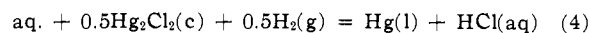
Precision temperature and concentration studies on this cell have been reported by a number of authors,[19−22] but the data of Das and Ives appear to be the most satisfactory. Using the heat capacity data of Kelley[16] and $\overline{C}_{p_2}°$ of HCl(aq) from this research, $E_{25}°$ was calculated from the Das and Ives[19] $E°_T$ values from 5 to 45° using eq. 1 and 3. The results of these calculations indicate that the presently accepted[8,23] value of $\Delta S°_{25} = -7.65$ cal. mole^{-1} deg.$^{-1}$ is not satisfactory; the present analysis gives $\Delta S°_{25} = -6.81$ cal. mole^{-1} deg.$^{-1}$ as the best value for eq. 4. Figure 3 summarizes the results of these calculations, wherein the two different values for $\Delta S°_{25}$ were compared. The best average value of $E°_{25}$ appears to be 0.268155 v. It is interesting to note that two other sets of data[20,21] gave $\Delta S°_{25}$ values of −6.83 and −6.91 cal. mole^{-1} deg.$^{-1}$ by a similar analysis, although there is somewhat greater spread in the resulting values of $E°_{25}$. We recommend adoption of $E°_{25} = 0.268155$ v. and $\Delta S°_{25} = -6.81$ cal. mole^{-1} deg.$^{-1}$ for the calomel electrode (eq. 4).

The discrepancy in the previously recorded entropies[8,23] and the value adopted for this cell are due to the poorly known entropy of calomel and also to the new

(17) This exact value of the entropy of chloride ion has also been verified by independent measurements on the heat and free energy of solution of HCl(g) by C. E. Vanderzee and J. D. Mutter, J. Phys. Chem., 67, 2521 (1963). This fact means that the best entropies based on the third law lead to the same value for $\Delta S°_{25}$ of the silver-silver chloride electrode that result from the present independent analysis based upon eq. 3. Consequently, the pure substances of cell reaction 2 must have no residual entropy at absolute zero; otherwise, eq. 3 would not lead to constant values of $E°_{25}$. This is one of the reasons for designating the present method of treating cell data as a "third-law" analysis.

(18) R. S. Greeley, W. T. Smith, M. H. Lietzke, and R. W. Stoughton, J. Phys. Chem., 64, 652 (1960).

(19) S. N. Das and D. J. G. Ives, J. Chem. Soc., 1619 (1962).

(20) R. S. Gupta, G. J. Hills, and D. J. G. Ives: see D. J. G. Ives and G. J. Janz, "Reference Electrodes," Academic Press, New York, N. Y., 1961, p. 138.

(21) G. J. Hills: see D. J. G. Ives and G. J. Janz, ref. 20.

(22) A. K. Grzybowski, J. Phys. Chem., 62, 555 (1958).

(23) D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Washington, D. C., 1956.
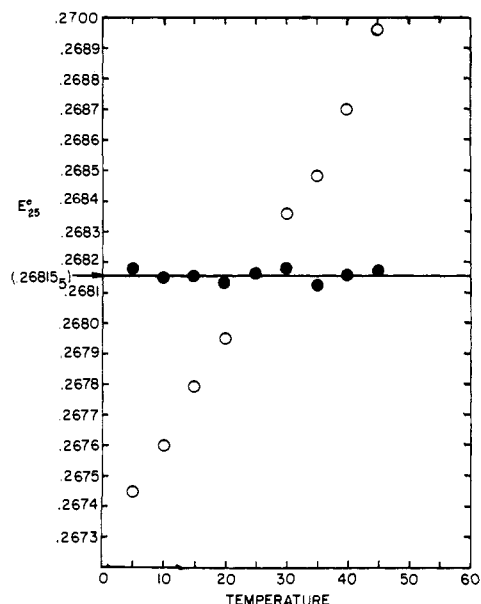
Fig. 3.—Third-law analysis of the calomel electrode: solid circles were calculated (eq. 1 and 3) using $\Delta S^\circ_{25} = -6.81$ cal. mole^{-1} deg.$^{-1}$, and open circles using $\Delta S^\circ_{25} = -7.65$ cal. mole^{-1} deg.$^{-1}$ (previously accepted value): the least-squares value of E°_{25} calculated from eq. 1 and 3 is 0.268155 v.

TABLE III

THIRD-LAW POTENTIALS OF THE CALOMEL ELECTRODE[a]

t, °C.	$E^\circ_{T(\text{obsd})}$, v.[b]	$\int_{298}^{T} \Delta C_p^\circ dT$, cal.	$T \int_{298}^{T} \Delta C_p^\circ \frac{dT}{T}$, cal.	E°_{25}, v.[c] (from col. 2)	E°_T, v.[d] (calcd.)
0		1124.8	1077.1		0.27347
5	0.27289	846.7	819.1	0.26818	0.27286
10	0.27191	615.4	600.0	0.26815	0.27192
15	0.27085	402.6	396.7	0.268155	0.27085
20	0.26956	199.2	198.05	0.26813	0.26958
25	0.26816	0.0	0.0	0.26816	0.268155
30	0.26661	−196.6	−198.7	0.26818	0.26659
35	0.26486	−391.85	−398.9	0.26812	0.26490
40	0.26304	−586.6	−602.3	0.26815	0.263045
45	0.26103	−781.2	−809.6	0.26817	0.26102
50		−976.7	−1021.0		0.25885
60		−1376.0	−1459.1		0.25422
70		−1793.2	−1925.9		0.24911
80		−2236.45	−2430.1		0.24352
90		−2711.5	−2980.1		0.23731
100		−3218.7	−3589.7		0.22992

[a] For the reaction $0.5Hg_2Cl_2(c) + 0.5H_2(g) + aq. = Hg(l) + HCl(aq)$. [b] Potential data are from ref. 19. [c] Using $\Delta S^\circ_{25} = -6.81$ cal. mole^{-1} deg.$^{-1}$ (eq. 3). [d] Using $\Delta S^\circ_{25} = -6.81$ cal. mole^{-1} deg.$^{-1}$ and $E^\circ_{25} = 0.268155$ v. (eq. 3).

value of the entropy of HCl(aq) at 25° proposed by this research. When these corrections are made, the recommended new entropy for Hg_2Cl_2 at 25° becomes $S^\circ_{25} = 45.82$ cal. mole^{-1} deg.$^{-1}$, changed from 46.8 cal. mole^{-1} deg.$^{-1}$. It should be noted that the present analysis depends upon a heat capacity equation for Hg_2Cl_2 based on some estimated data in this temperature range.[16] However, such an estimation can be used with some confidence since the calculations are not as sensitive to errors in ΔC_p° as they are to errors in ΔS°_{25}. This fact can be seen by a perusal of the data of Table III, where the two integrals involving ΔC_p° can be seen to partially cancel themselves over limited temperature ranges.

Using the above recommended values for the calomel electrode, third-law potentials have been calculated from 0 to 100°. A summary of the pertinent calculations and these potentials are given in Table III.

The data of Tables II and III illustrate rather well the difficulties in attempting to obtain reliable infor-

mation on the heat capacity behavior of cells and electrolytes from temperature coefficient studies alone. The heat capacity effect comes about as essentially a correction to the heat and entropies. Since these carry opposite signs in the relation $\Delta F = \Delta H - T\Delta S$, the resulting free energies and potentials always depend upon the *differences* between the two ΔC_p terms in eq. 1. The values of the two integrals are rather sizeable, as can be seen in Tables II and III, but the differences are much smaller. To attempt to obtain reliable information on ΔC_p° by working backwards through the difference functions from the E°_T data is not feasible.[24] It is far better to use the proposed third-law analysis, even if the $C_{p_2}^\circ$ values for the electrolyte are not known and must be estimated over the temperature range involved. The estimation of reliable $\overline{C_{p_2}}^\circ$ values as functions of temperature will be the subject of the following papers of this series.

(24) It can be shown that a six- or seven-term power series expression for cell potentials as a function of temperature would be required to correctly approximate the true ΔC_p behavior.